

Synthesis and photophysical properties of chiral 1,7-7',1'-cyclopyrenylene oligomers

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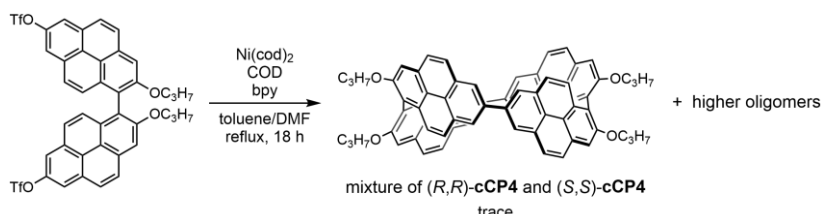
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Arylene macrocycles constitute one of the most important shape-persistent oligomers. Pyrene is a unique polycyclic aromatic hydrocarbon among those building units for larger cycloarylenes because of its highly emissive property and large π -surface. Previously, we have reported a series of directly linked 1,8- or 4,10-cyclic pyrene oligomers with intriguing properties, such as ring-strain-driven reaction,¹ the incorporation of guest molecules,² macrocyclic chirality with an odd number of pyrene unit,³ and structural conversion upon heating.⁴

In order to make a rigid chiral framework based on cyclopyrenylene, Ni-mediated coupling reaction of a 1,1'-bipyrenyl with trifluoromethanesulfonyloxy groups at 7 and 7' positions was performed and gave a series of chiral 1,7-7',1'-cyclic pyrene oligomers **cCP_n** (Scheme 1). Cyclic tetramer **cCP4** is a chiral molecule and is expected to produce CPL-CT emission through host-guest interaction with an achiral acceptor molecule. Actually, the fluorescence spectrum of the complex of **cCP4** with 1,2,4,5-tetracyanobenzene (TCNB) in the solid state showed a large redshift, confirming the formation of the CT complex (Figure 1). The interaction between **cCP_n** and various electron-deficient guest molecules has been evaluated for their photophysical properties.



Scheme 1. Synthesis of **cCP_n** with Ni(cod)₂.

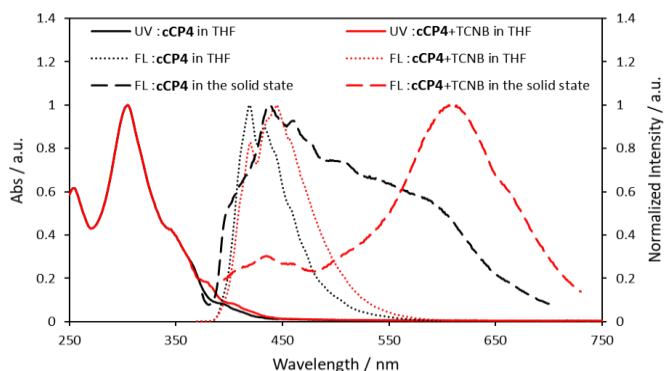


Figure 1. UV-vis and fluorescence spectra of **cCP4** with and without TCNB.

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3) R. Kurosaki, et al. *Chem. Lett.* **2020**, *49*, 892. 4) R. Kurosaki, et al. *Chem. Eur. J.* in revision.